CHEMISTRY LETTERS, pp. 903-906, 1986.

SYNTHESIS OF ETHYLENE BY PARTIAL OXIDATION OF METHANE OVER THE OXIDES OF TRANSITION ELEMENTS WITH LiCl

Kiyoshi OTSUKA,* Qin LIU, Masaharu HATANO, and Akira MORIKAWA
Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152

The synthesis of ethylene directly from methane has been tested in the presence of oxygen over the LiCl-added transition metal oxides. The oxides of Mn and Ni with LiCl produced ethylene with high selectivity (ca. 60%) and yield (ca. 27%) under the following experimental conditions: T=1023 K, $P(CH_4)/P(O_2)=2/1$, $P(CH_4)=5.1$ kPa, and W/F=600-1200 g l^{-1}s.

Although there exist abundant reserves of natural gas (essentially methane), no efficient process to convert methane directly into more valuable chemicals such as ethylene and methanol has been found yet. Because of the high stability of methane, it has to be processed through a previous steam reforming step in any route to the desired chemicals. Obviously, the direct synthesis of ethylene or methanol by partial oxidation of methane would be a very desirable process. However, only a few fundamental work has been reported on the catalytic conversion of methane into higher hydrocarbons.$^{1-5)}$

We have already reported that methane can be converted directly to ethylene over the $LiCl/Eu_2O_3$, $LiCl/Sm_2O_3$, LiCl/MgO, and $NaCl/Eu_2O_3$ with high yields of ethylene 17.2, 16.8, 16.8, and 16.2%, respectively.$^{6)}$ The presence of chlorides of Li and Na enhanced the catalytic activities of the metal oxides in the formations of C_2-compounds (C_2H_4 + C_2H_6) and especially increased the selectivity to C_2H_4. The high C_2H_4/C_2H_6 ratio in the C_2-products is of great advantage because no subsequent conversion of C_2H_6 into C_2H_4 is required. Thus, the catalysts converting CH_4 into C_2H_4 with higher selectivity and yield are strongly desired. In this communication we describe the results of the one-pass conversion of methane to ethylene on the catalysts which have better selectivities and yields than the catalysts described above.

Powder metal oxides of the first transition elements in the periodic table were used as catalysts. The initial compositions of the oxides used were TiO_2, Cr_2O_3, MnO_2, Co_3O_4, NiO, CuO, and ZnO. The oxides with LiCl were prepared by impregnation method using aqueous solution of the chlorides. The content of LiCl was adjusted to 20 mol% for each LiCl/oxide catalyst. The catalysts were pretreated in air at 973 K for 2 h before use. The Li_2CO_3/Ni-oxide and Li_2O/Ni-oxide (Li 20 mol%) were prepared in a similar way as above. The latter catalyst was prepared by decomposition of the $LiNO_3$ added to NiO at 973 K in air. The experiments were carried out using a conventional gas-flow system at atmospheric pressure. A reacting gas mixture of CH_4, O_2, and He (a diluent) was introduced to a fixed bed flow reactor. The reaction conditions were as follows; T=1023 K, $P(CH_4)$=5.1-60.8 kPa, $P(CH_4)/P(O_2)$=2/1, weight of catalyst = 1.00 g, and W/F=600 g l^{-1}s.

The catalytic activities and selectivities to the C_2-compounds (C_2H_4 + C_2H_6) were examined first for the transition metal oxides without LiCl. The oxides produced only CO, CO_2, and H_2O without any C_2-compounds and higher hydrocarbons. The addition of LiCl to the oxides exerted a remarkable effect on the conversion of methane to the C_2-compounds. Table 1 shows the conversions of CH_4 and O_2, the selectivities of C_2H_4 and C_2H_6, and the yields of C_2-compounds (C_2H_4 + C_2H_6) and C_2H_4 observed for the metal oxides with LiCl at a time on stream 20 min. The pressure of methane at the inlet of the reactor was 5.1 kPa. As can be seen in Table 1, high conversion of CH_4 and high selectivities to the C_2-compounds (C_2H_4 + C_2H_6), accordingly the high C_2-yields, were observed for the oxides of Ti, Mn, Co, Ni, Cu, and Zn in the presence of LiCl. A striking effect of LiCl was on the selectivity to C_2H_4. The percentage of C_2H_4 in the C_2-compounds produced were higher than 90% for the LiCl-added oxides of Ti, Mn, Co, Ni and Cu.

The effect of the pressure of CH_4 and O_2 on the conversion, selectivities, and yields for the LiCl/Mn-oxide were shown in Table 2. The conversion of O_2 was higher than 95% at any pressures in Table 2. The conversion of CH_4 were very high (>36%) at any pressures tested. The C_2-selectivity (C_2H_4 + C_2H_6) was held at higher values than 50% when the pressure of reactants were less than 0.7 atm.

Table 1. Ethylene from methane over LiCl/transition metal oxides

Catalyst	CH_4-conversion %	O_2-conversion %	C_2H_4-selectivity %	C_2H_6-selectivity %	C_2-yield %	C_2H_4-yield %
LiCl/Ti-oxide	17.6	40	77.1	5.7	14.6	13.6
LiCl/Cr-oxide[a]	26.1	85	0	0	0	0
LiCl/Mn-oxide	47.3	95	59.4	5.3	30.6	28.1
LiCl/Fe-oxide	22.2	92	0	0	0	0
LiCl/Co-oxide[a]	48.0	91	32.1	3.4	17.0	15.4
LiCl/Ni-oxide	25.9	57	56.2	15.6	18.6	14.5
LiCl/Cu-oxide[a]	49.5	80	20.6	0	10.2	10.2
LiCl/Zn-oxide	22.0	49	42.6	26.3	15.2	9.4

a) Excess oxygen was observed in outlet gas (the sum of the unreacted oxygen and the oxygen in CO, CO_2, and H_2O) compared to the oxygen in inlet gas, indicating the reduction of the metal oxides.

Table 2. Effect of the pressure of reactants on partial oxidation of CH_4 over LiCl/Mn-oxide

Pressure of reactants atm	CH_4-conversion %	C_2H_4-selectivity %	C_2H_6 selectivity %	C_2-yield %	C_2H_4-yield %
0.07	47.3	59.4	5.3	30.6	28.1
0.14	40.8	54.9	9.3	26.2	22.4
0.28	38.8	46.8	11.7	22.7	18.2
0.42	36.8	42.5	11.6	19.9	15.6
0.56	36.0	40.1	11.6	18.6	14.4
0.70	41.2	39.8	13.0	21.8	16.4
0.84	41.7	28.7	14.1	17.8	12.0

Table 3. Effect of the pressure of reactants on partial oxidation of CH_4 over LiCl/Ni-oxide

Pressure of reactants atm	CH_4-conversion %	C_2H_4-selectivity %	C_2H_6 selectivity %	C_2-yield %	C_2H_4-yield %
0.07	43.1	60.9	6.2	28.9	26.2
0.14	41.9	56.5	6.7	26.5	23.7
0.28	37.8	51.6	6.5	22.0	19.5
0.42	41.8	44.1	9.2	22.3	18.4
0.56	40.5	46.2	7.6	21.8	18.7
0.70	39.4	36.3	8.9	17.8	14.3

Table 4. Effects of Li_2CO_3 and Li_2O on partial oxidation of CH_4 over Ni-oxide

Catalyst	CH_4-conversion %	O_2-conversion %	C_2H_4-selectivity %	C_2H_6-selectivity %	C_2-yield %	C_2H_4-yield %
Li_2CO_3	25.9	70	26.5	22.4	12.7	6.9
Li_2O	26.1	75	23.8	32.0	14.6	6.2

Table 3 shows the effect of pressure of the reactants on the reaction over LiCl/Ni-oxide under the same experimental conditions in Table 2 except the weight of catalysts used. Since the conversion of oxygen for the LiCl/Ni-oxide shown in Table 1 was low (57%), the weight of catalyst was increased to 2.0 g (W/F=1200 g l^{-1}s) in Table 3. Equally high C_2H_4-selectivity and accordingly high C_2H_4-

yield compared to the results in Table 2 are indicated in Table 3. The yields of C_2H_4 were maintained at higher values (>18%) at the pressure of reactants less than 0.56 atm.

Table 4 shows the effects of Li_2CO_3 and Li_2O added to NiO on the conversions, selectivities, and yields. The reaction conditions were same as in Table 1. The results in Table 4 show that the addition of Li_2CO_3 and Li_2O improved remarkably the formations of C_2-compounds because only deep oxidation occurred over Ni-oxide in the absence of the lithium compounds. These observations may suggest that the presence of lithium in the oxides generate new active sites effective to the dehydrogenation and coupling of CH_4. More important is the depression of deep oxidation of CH_4 and C_2-hydrocarbons by the lithium compounds. The Li_2CO_3 and Li_2O, however, did not produce C_2H_4 selectively in contrast to LiCl (see LiCl/Ni-oxide in Table 1). The ratios of C_2H_4/C_2H_6 in the C_2-products were less than 1.2 for the Li_2CO_3/Ni-oxide and Li_2O/Ni-oxide. Thus, it is obvious that LiCl has a specific ability to improve the selectivity to C_2H_4.

The favorable effect of the Li-compounds added to the oxides can be ascribed to the depression of the deep oxidations of CH_4 and C_2-hydrocarbons. The specific effect of LiCl to improve the selectivity to C_2H_4 might be ascribed to the abstraction of hydrogen from C_2H_6 by liquid LiCl on the surface or by the vapor of LiCl (melting point of LiCl is 883 K). The higher melting points of Li_2CO_3 and Li_2O (996 and 1993 K, respectively) compared to LiCl may not allow the former additives to have such ability. Alternatively, LiCl may play a role in supplying chlorine radicals. The chlorine radicals are known to catalyze the formations of C_2H_4 from CH_4 in gas phase.7)

The deactivation of catalysts with reaction time were examined for the LiCl/Ni-oxide and LiCl/Mn-oxide. The catalytic activities and product distribution did not change appreciably within 2 h. However, the C_2H_4-selectivity decreased sharply after 2 h, though the conversions of CH_4 and O_2 did not change appreciably. Deposition of LiCl at the outlet of the reactor was observed during the reaction. These observations suggest that the chlorine atoms in the catalysts diminish with time by evaporation, decomposition, and reaction with the reactants. Further studies are needed to describe the mechanism of decrease of LiCl and the role of LiCl in catalysis in detail.

References

1) G.E. Keller and M.M. Bhasin, J. Catal., 73, 9(1982).
2) W. Hinsen, W. Bytyn, and M. Baerns, Proc. 8th Int. Congr. Catal.,3, 581(1984).
3) T. Ito, Ji-Xiang Wang, Chiu-Hsun Lin, and J.H. Lunsford, J. Am. Chem. Soc., 107, 5062(1985).
4) K. Otsuka, K. Jinno, and A. Morikawa, Chem. Lett., 1985, 499.
5) K. Otsuka, Qin Liu, M. Hatano, and A. Morikawa, Chem. Lett., 1986, 467.
6) K. Otsuka, Qin Liu, and A. Morikawa, submitted for publication.
7) M. Weissman and S.W. Benson, Intern. J. Chem. Kinet., 16, 307 (1984).

(Received March 7, 1986)